

Received: June 10, 1989; accepted: September 11, 1989

(α -PERFLUOROHEPTYL- β,β -DICYANOVINYL)AMINOSTYRENES: A NOVEL CLASS OF PERFLUOROCARBON-SOLUBLE DYES [1]

BETHANY K. FREED and W. J. MIDDLETON*

Chemistry Department, Ursinus College, Collegeville, Pennsylvania 19426 (U.S.A.)

SUMMARY

Several examples of (α -perfluoroheptyl- β,β -dicyanovinyl)aminostyrenes (**3**), a novel class of perfluorocarbon-soluble dyes, were prepared by the reaction of 2-chloro-1,1-dicyano-2-(perfluoroheptyl)ethylene (**2**) with aromatic amines. The ethylene **2** was prepared from methyl perfluorooctanoate, malononitrile, and phosphorus pentachloride. The λ_{max} for perfluorohexane solutions of the dyes ranges from 419 nm for the dye prepared from *N*-phenylmorpholine to 490 nm for the dye prepared from julolidine.

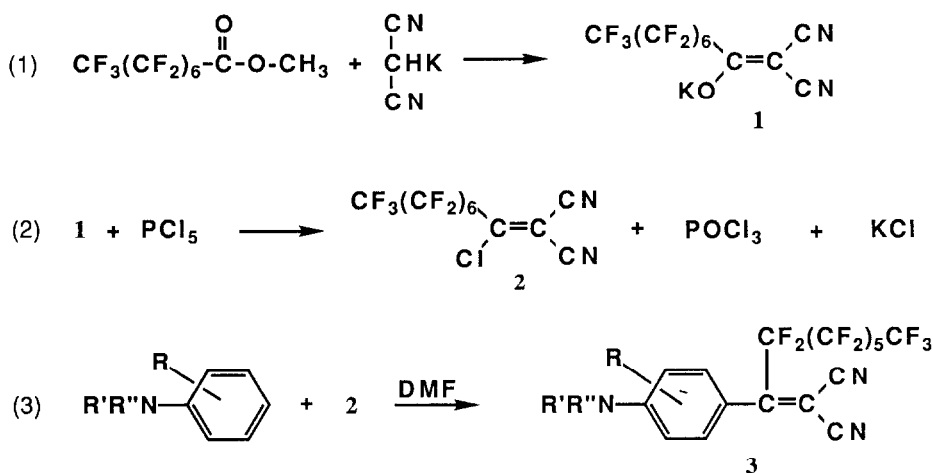
INTRODUCTION

Chlorofluorocarbons are efficient and inexpensive fluids used in most refrigeration and air conditioning units. In the last few years, it has been realized that their use presents a serious environmental hazard, and it is probable that their production will eventually be prohibited by law [2]. Fluorocarbons or hydrofluorocarbons (compounds containing only carbon, hydrogen, and fluorine such as $\text{CF}_3\text{CH}_2\text{F}$) appear to be environmentally safe, and are one of only a few acceptable substitutes for chlorofluorocarbons in mobile air conditioning units [3]. Unfortunately, these substitutes are many times more expensive than the relatively inexpensive chlorofluorocarbons. For this reason, an efficient early warning leak detection system is needed, so leaks that are common in automobile air conditioning units can be detected and stopped before the expensive fluid is lost. Soluble dyes have been developed for leak detection purposes in air conditioning units that utilize chlorofluorocarbons, but these dyes have not been widely used because chlorofluorocarbons are inexpensive. Unfortunately, these dyes will not function in systems that utilize fluorocarbons, because the dyes are not soluble in these very non-polar fluids. Our goal was to synthesize a series of new fluorocarbon-soluble dyes, utilizing chemistry developed earlier by one of us [4].

*To whom correspondence should be addressed.

DISCUSSION AND RESULTS

Nine (α -perfluoroheptyl- β,β -dicyanovinyl)aminostyrenes (**3a-i**, TABLE I) were prepared by the series of reactions represented in *Scheme 1*. First, the potassium salt of malononitrile was condensed with methyl perfluorooctanoate in ethanol to give the potassium salt of β,β -dicyano-vinyl- α -(perfluoroheptyl)vinyl alcohol (**1**) in nearly quantitative yield. The anhydrous salt **1** was then treated with phosphorus pentachloride to give a moderate yield of 2-chloro-1,1-dicyano-2-(perfluoroheptyl)ethylene (**2**). The dyes (**3**) were prepared by reaction of **2** with an appropriate aromatic amine in dimethylformamide solvent. A α -perfluoroheptyl- β,β -dicyanovinyl derivative of 6-(dimethylamino)fulvene (**4**, TABLE I) was also prepared in a similar manner from **2** and 6-dimethylaminofulvene.

*Scheme 1*

All of these dyes (**3a-i** and **4**) had good solubility in the extremely nonpolar solvent, perfluorohexane. For comparison, three related dyes (**5a,b,c**, TABLE I) that contain a trifluoromethyl group in place of the perfluoroheptyl group were prepared by reaction of 2-chloro-1,1-dicyano-2-(trifluoromethyl)ethylene [4] with aromatic amines. The trifluoromethyl dyes were considerably less soluble in perfluorohexane; only the less crystalline **5b** prepared from *N,N*-diethylaniline was sufficiently soluble so that a UV-visible spectrum could be obtained. One example of a dye (**6**, TABLE I) that contained the heptafluoropropyl group was prepared from 2-chloro-1,1-dicyano-2-(heptafluoropropyl)ethylene [4] and *N,N*-dimethylaniline. As expected,

this dye appeared to have a solubility in perfluorohexane that was between that of the corresponding dyes that contained the trifluoromethyl group (**5a**) and the perfluoroheptyl group (**3a**).

The size of the perfluoroalkyl group in this series of dyes has a marked effect on their solubility, but it appears to have only a small effect on the wavelength of maximum intensity absorption (λ_{max}). For example, the λ_{max} of **5a** (with CF_3), **6** (with $\text{CF}_2\text{CF}_2\text{CF}_3$), and **3a** (with perfluoroheptyl) in acetone all fall within the narrow range of 9 nm (Fig. 1). It should be noted, however, that the perfluoroalkyl group has an appreciable effect on the λ_{max} when compared with other substituents in the same position, such as H [5], CO_2Et , or CN [6]. This can be seen by comparing the λ_{max} in acetone of **3a**, **5a**, **6**, **7**, **8** and **9** (Figure 1).

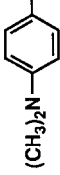
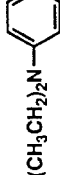
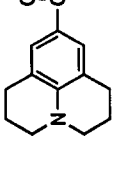


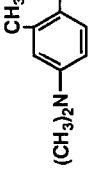

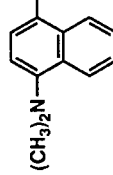
	X	$\lambda_{\text{max}}^{\text{acetone}}$
3a	$\text{CF}_3(\text{CF}_2)_6$	493
5a	CF_3	484
6	$\text{CF}_3\text{CF}_2\text{CF}_2$	490
7	H [5]	432
8	CO_2Et [6]	453
9	CN [6]	521

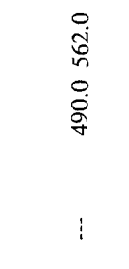
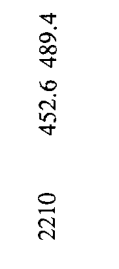
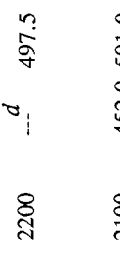
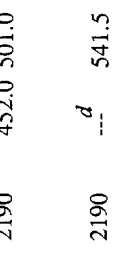
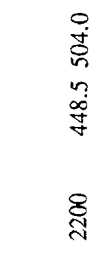
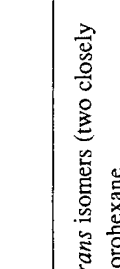
Fig. 1.

The (α -perfluoroheptyl- β,β -dicyanovinyl)aminostyrenes prepared in this study show moderate tinctorial strength (eg., **3a** in acetone at λ 493 nm, $\epsilon = 16,500 \text{ Lmol}^{-1}\text{cm}^{-1}$) and range in color from pale yellow (in perfluorohexane) for **3d** to cherry red (in acetone) for **3a** to a deep purple (in DMSO) for **3c**. In general, there appears to be a correlation between the λ_{max} of the dye and the basicity of the aniline used for its preparation; the more basic the aniline, the longer the λ_{max} . For example, **3a**, prepared from *N,N*-dimethylaniline (pKa, 5.15) absorbs at 450.5 nm (perfluorohexane), whereas **3b**, prepared from the more basic *N,N*-diethylaniline (pKa, 6.61) absorbs at the longer wavelength of 464.5 nm (perfluorohexane), and *N*-phenylmorpholine and *N,N*-di(2-chloroethyl)aniline, the least basic anilines in this study, gave dyes that absorb at much shorter wavelengths. This correlation may not hold for all of the dyes prepared in this study; the relative basicities of some of the anilines are not known to us, and steric effects may also be important.

There also appears to be a correlation between the basicity of the aniline and the rate of reaction of the aniline with the chloroethylene **2**. An intense color forms immediately when *N,N*-dimethylaniline or julolidine is mixed with **2** in DMF, but the color requires several seconds to develop when the less basic *N*-phenylmorpholine or *N,N*-di(2-chloroethyl)aniline is used.

TABLE I
 α -Perfluoroalkyl- β,β -dicyanovinyl Dyes

No.	Dyes		Yield %	Analysis, F		mp °C	IR, cm^{-1} (CN)	λ_{max} , nm	
	Structure	Formula		Calcd	Found			C_6F_{14}	DMSO
3a		$\text{C}_{19}\text{H}_{10}\text{F}_{15}\text{N}_3$	84	50.41	50.09	85-90	2220	450.5	508.0
3b		$\text{C}_{21}\text{H}_{14}\text{F}_{15}\text{N}_3$	85	48.03	47.87	^a -----	2210	464.5	517.5
3c		$\text{C}_{23}\text{H}_{14}\text{F}_{15}\text{N}_3$	77	46.16	46.17	125-7	2210	490.4	556.2
3d		$\text{C}_{21}\text{H}_{12}\text{F}_{15}\text{N}_3\text{O}$	36	46.92	46.82	105-8	2200	419.0	463.5
3e		$\text{C}_{21}\text{H}_{12}\text{F}_{15}\text{N}_3$	56	48.19	47.81	121-4	2200	463.0	506.0
3f		$\text{C}_{20}\text{H}_{12}\text{F}_{15}\text{N}_3$	24	49.19	48.89	^a -----	2210	447.5	499.4
3g		$\text{C}_{21}\text{H}_{12}\text{Cl}_2\text{F}_{15}\text{N}_3$	40	43.03	42.72	^a -----	---	414.5	480.0
3h		$\text{C}_{23}\text{H}_{12}\text{F}_{15}\text{N}_3$	42	46.31	46.26	225-7	2200	438.5	470.5

<div style="text-align: center;">  <p>3 i</p> </div>	<div style="text-align: center;"> $C_{25}H_{17}F_{15}N_4$ </div>	<div style="text-align: center;"> 18 </div>	<div style="text-align: center;"> 43.28 42.92 ^a --- </div>	<div style="text-align: center;"> 490.0 562.0 </div>
<div style="text-align: center;">  <p>4</p> </div>	<div style="text-align: center;"> $C_{19}H_{10}F_{15}N_3$ </div>	<div style="text-align: center;"> 34 </div>	<div style="text-align: center;"> 50.41 50.22 135-6 </div>	<div style="text-align: center;"> 2210 452.6 489.4 </div>
<div style="text-align: center;">  <p>5 a</p> </div>	<div style="text-align: center;"> $C_{13}H_{10}F_3N_3$ </div>	<div style="text-align: center;"> 85 </div>	<div style="text-align: center;"> --- --- 116-18 </div>	<div style="text-align: center;"> ^d --- 497.5 </div>
<div style="text-align: center;">  <p>5 b</p> </div>	<div style="text-align: center;"> $C_{15}H_{14}F_3N_3$ </div>	<div style="text-align: center;"> -- </div>	<div style="text-align: center;"> 19.43 19.03 ^a --- </div>	<div style="text-align: center;"> 2190 452.0 501.0 </div>
<div style="text-align: center;">  <p>5 c</p> </div>	<div style="text-align: center;"> $C_{17}H_{14}F_3N_3$ </div>	<div style="text-align: center;"> -- </div>	<div style="text-align: center;"> 17.96 18.09 120-3 </div>	<div style="text-align: center;"> 2190 ^d --- 541.5 </div>
<div style="text-align: center;">  <p>6</p> </div>	<div style="text-align: center;"> $C_{15}H_{10}F_7N_3$ </div>	<div style="text-align: center;"> -- </div>	<div style="text-align: center;"> 36.41 36.21 ^a --- </div>	<div style="text-align: center;"> 2200 448.5 504.0 </div>

^a Obtained as a viscous liquid or an amorphous glass. ^b Presumed mixture of *cis* and *trans* isomers (two closely spaced spots by TLC, silica-ether/pentane) ^c Reference [4]. ^d Insoluble in perfluorohexane.

EXPERIMENTAL

Potassium Salt of β,β -dicyano- α -(perfluoroheptyl)vinyl Alcohol (1)

A solution of 3.30 g (0.05 mol) of malononitrile in 7.0 mL ethanol was added to a solution prepared by dissolving 2.00 g (0.05 mol) of potassium in 37.5 mL of ethanol. Methyl perfluorooctanoate, 21.4 g (0.05 mol), was added dropwise and the resulting solution was allowed to stir for a minimum of two hours. The reaction mixture was then evaporated to dryness under reduced pressure to give 25.0 g (100 %) of **1** as an off-white solid: IR (Nujol) 2200 and 2240 cm^{-1} (CN) and 1655 cm^{-1} (C=C); Anal. Calcd for $\text{C}_{11}\text{F}_{15}\text{KN}_2\text{O}$: F, 56.97. Found: F, 56.59.

2-Chloro-1,1-dicyano-2-(perfluoroheptyl)ethylene (2)

A mixture of 50.0 g (0.1 mol) of **1** and 20.8 g (0.1 mol) phosphorus pentachloride was heated in a simple still. Phosphorus oxychloride was collected from 90° to 116°. When no further distillation occurred, heating was discontinued. The system was then placed under reduced pressure and heating was resumed. A volatile crystalline solid began forming inside the still and was driven into a cooled receiver using a heat gun. The product which still contained some POCl_3 was further purified by sublimation at 0.025 mm Hg to give 11.51 g (24 % yield) of **2** as a crystalline white solid: mp 48-55°; IR (Nujol) 2230 cm^{-1} (CN); Anal. Calcd for $\text{C}_{11}\text{ClF}_{15}\text{N}_2$: F, 59.30; N, 5.83. Found: F, 59.27; N, 5.75.

Preparation of 4-(Amino)- α -(perfluoroalkyl)- β,β -dicyanostyrenes (Table I)

The dyes listed in Table I were prepared by the following general procedure: A solution of 1.5 mmol of the substituted aniline in 1 mL *N,N*-dimethylformamide was added dropwise to a small vial containing 1.5 mmol of a 2-chloro-1,1-dicyano-2-(perfluoroalkyl)ethylene. An intense color developed upon mixing. Fluorotrichloromethane, 50-100 mL, was added and the resulting mixture was washed with three 50 mL portions of deionized water, dried (MgSO_4), and then evaporated under reduced pressure to give the dye in analytically pure form. In some instances, a small amount of chromatography grade silica was added to the fluorotrichloromethane before filtration in order to obtain a purer product.

4-(*N,N*-dimethylimino)- α -(perfluoroheptyl)- β,β -dicyanostyrene (3a) was prepared from *N,N*-dimethylaniline and the chloroethylene **2**; **4-(*N,N*-diethylamino)- α -(perfluoroheptyl)- β,β -dicyanostyrene (3b)** was prepared from *N,N*-diethylaniline and **2**; **9-(α -(perfluoroheptyl)- β,β -dicyanovinyl)julolidine (3c)** was prepared from julolidine and **2**; **4-(4-morpholino)- α -(perfluoroheptyl)- β,β -dicyanostyrene (3d)** was prepared

from *N*-phenylmorpholine and **2**; **1-pyrrolidino- α -(perfluoroheptyl)- β,β -dicyanostyrene (3e)** was prepared from *N*-phenylpyrrolidine and **2**; **4-(*N,N*-dimethylamino)-2-methyl- α -(perfluoroheptyl)- β,β -dicyanostyrene (3f)** was prepared from *N,N*-dimethyl-*m*-toluidine and **2**; **4-[*N,N*-di(2-chloroethyl)amino]- α -(perfluoroheptyl)- β,β -dicyanostyrene (3g)** was prepared from *N,N*-di(2-chloroethyl)aniline and **2**; **1-*N,N*-dimethylamino-4-(α -perfluoroheptyl)- β,β -dicyanovinyl)naphthalene (3h)** was prepared from 1-dimethylaminonaphthalene and **2**; **1,8-bis(*N,N*-dimethylamino)-4-(α -perfluoroheptyl)- β,β -dicyanovinyl)naphthalene (3i)** was prepared from 1,8-bis(dimethylamino)naphthalene and **2**; **6-(dimethylamino)-2-(α -perfluoroheptyl)- β,β -dicyanovinyl)fulvene (4)** was prepared from 6-dimethylaminofulvene and **2**; **4-(*N,N*-dimethylamino)- α -(trifluoromethyl)- β,β -dicyanostyrene (5a)** was prepared from *N,N*-dimethylaniline and 2-chloro-1,1-dicyano-2-(trifluoromethyl)ethylene [4]; **4-(*N,N*-diethylamino)- α -(trifluoromethyl)- β,β -dicyanostyrene (5b)** was prepared from *N,N*-diethylaniline and 2-chloro-1,1-dicyano-2-(trifluoromethyl)ethylene; **9-(α -trifluoromethyl)- β,β -dicyanovinyl)julolidine (5c)** was prepared from julolidine and 2-chloro-1,1-dicyano-2-(trifluoromethyl)ethylene; and **4-(*N,N*-dimethylamino)- α -(heptafluoropropyl)- β,β -dicyanostyrene (6)** was prepared from *N,N*-dimethylaniline and 2-chloro-1,1-dicyano-2-(heptafluoropropyl)ethylene [4]. Compounds **1**, **2**, **3a-i**, **4**, **5b**, **5c**, and **6** are new compounds.

ACKNOWLEDGEMENTS

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Van Sant Research Fund of Ursinus College for support of this research.

REFERENCES

- 1 Portions of this paper were presented at the 43rd Intercollegiate Student Chemists Convention, Elizabethtown College, Elizabethtown, Pa. 17022, U.S.A., April 8, 1989.
- 2 M. D. Lemonick, *Time*, January 2, 1989, pp. 36-39; May 15, 1989, p. 63.
- 3 L. R. Ember, P. A. Layman, W. Lepkowski, and P. S. Zurer, *Chem. and Eng. News*, November 24, 1986, pp. 14-64; P. Zurer, *Chem. and Eng. News*, April 24, 1989, p. 6.
- 4 W. J. Middleton and E. M. Bingham, *J. Fluorine Chem.*, **20**, (1982) 397.
- 5 F. Sachs and W. Lewin, *Ber.*, **35**, (1902) 3569.
- 6 B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman and H. F. Mower, *J. Am. Chem. Soc.*, **80**, (1958) 2806.